

STRUCTURAL MORPHOLOGY AND THERMAL PROPERTIES OF POLYPROPYLENE/BARIUM CARBONATE NANOCOMPOSITES

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ABSTRACT

Incorporation of nanoparticle metallic carbonates in thermoplastic polymers like polypropylene has been done for decades to make the composites having remarkable and enhanced properties. An attempt has been made in this way, in order to enhance thermal properties of the composite materials. Structural morphology and thermal properties of high density polypropylene reinforced with Barium carbonate nano particles with filler loadings of 1%, 3%, 5% & 10% wt. of polypropylene (PP) nano composites have been studied. A good dispersion of nano particles is found in SEM micrographs for the composite PP+5% BaCo₃. Results of DSC thermal studies have revealed a considerable improvement in the percentage of cry stallinity and a good thermal stability at the BaCo₃ filler loading of 5% wt. of PP when compared to other nano composites.

KEYWORDS: Nano Composites, Barium Carbonate Nano Particles, Polypropylene & Thermal Properties

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INTRODUCTION

There has been a quest for decades in designing light weight and high strength materials. When compared to traditional materials, polymer nanocomposites exhibit changes in some properties at very low filler loadings like carbon nanotubes [1, 2] and graphite nanoplatelets [3-6]. The desired properties can be achieved only when there is a homogeneous dispersion of nano fillers in the polymer matrix and good adhesion between nano fillers and host polymer matrix [7]. In fact the desired properties of the composites filled micron-sized filler particles are not adequate to those filled with micro particles of same filler [8, 9]; also physical, mechanical and thermal properties cannot be achieved by using conventional micron-sized particles.

Due to the significant improvement in mechanical properties, thermal stability and electrical properties over the conventional thermoplastic polymers, polymer nanocomposites have been attracting the attention for few decades [10]. The effect of filler nanoparticles on these properties have been studied extensively [11]. Stress concentration, de-bonding of polymer/ filler interface and formation of shear bonds is the key mechanism of toughening the thermoplastic polymers incorporated with inorganic fillers. The inorganic filler acts as stress concentrator in the polymer matrix during the deformation because of the difference between elastic behaviors of the phases, i.e. each phase has a different elastic modulus [13]. Based on which, layered silicates, such as montmorillonite, has been used [14-17]. Nanocomposites prepared using montmorillonite showed improved strength, modulus and heat distortion temperature properties. Even though attractive improvements in physical and mechanical properties of the polymer/ clay nanocomposites have been noted, a significant drawback of low fracture toughness became a hindrance for engineering applications. In many cases, a considerable decrease in

toughness due to the incorporation of clay has been reported. This has put a major challenge in research of toughening polymers. Nanocomposites have also been prepared using silica [18, 19] and Calcium carbonate [20-23]. Among all, Calcium carbonate has been one of the most commonly used inorganic fillers for thermoplastics, such as polyethylene (PE), poly vinyl chloride and polypropylene (PP).

PP is the most commonly used commodity plastic which has the highest growth rate [24]. Among several fillers CaCO_3 is the most commonly used inorganic fillers in thermoplastic polymer like PP. Its composites find wide range of applications like sewer pipes, garden furniture etc; it has been reported that addition of Calcium carbonate nanoparticles could able to improve thermal and mechanical properties of polypropylene [25]. In early work of chan et al, [26] studies of mechanical and thermal properties of nano- CaCO_3 filled PP were reported. Here a new study has been carried out with the incorporation of nanoparticle Barium carbonate (NPBC) to isotactic polypropylene with filler loadings of 1%, 3%, 5% & 10% wt. of polypropylene. In this study morphological and thermal properties of nanoparticle BaCO_3 filled with PP were investigated. Structural morphology was investigated by using Scanning electron microscopy (SEM), where as thermal properties were carried out by Thermo gravimetric analysis (TGA) and Differential scanning calorimetry (DSC).

EXPERIMENTAL

MATERIAL AND METHODS

The powdered form of nano particle BaCO_3 and NPBC+PP nano composites with NPBC filler loadings of 1%, 3%, 5% & 10% weight of polypropylene were prepared to verify the effect of filler content and to investigate the relationships between is tactic polypropylene and Barium carbonate nano particle combinations. The polymer matrix material that used in this study is a commercial grade is tactic polypropylene supplied by SIGMA-ALDRICH, USA.

Preparation of BaCO_3 Nano Powder

For the preparation of BaCO_3 nano powder 0.1M BaCO_3 (100ml) aqueous solution was mixed with of Sodium bicarbonate (100ml) and stirred for 2 hours and washed with water for four times using centrifuge at 5000 rpm later it was dried at 60°C to obtain the required nano particle BaCO_3 powdered form. By the Scherer's formula it has been confirmed that the average particle size of BaCO_3 is in nano metric scale.

Preparation of BaCO_3 +Polypropylene Nanocomposites

Processing technique plays a vital role to achieve the desired improvement in the properties of interest. The processing technique employed is to disperse the filler in polymer matrix which has very strong tendency to agglomerate in the matrix due to their high surface energies. There are two common melt processing techniques to synthesis nanocomposites are melt- mixing using internal mixer and melt-extrusion using a twin-screw extruder. It has been reported that nanocomposites of PP with nano-sized CaCO_3 have been successfully prepared via melt-mixing by Chan et, al[26]; filler dispersion obtained has been found to be good by using the internal mixer and which has resulted in significant improvement in modulus and impact strength with only slightly lowering of the tensile strength. For higher filler loadings more than 10% weight of PP, the extrusion technique is more effective to disperse the nano filler resulting in better impact properties [27]. The present studies have been carried out with the filler loadings $\leq 10\%$ wt. of the polymer. Hence the internal mixer method has been employed for the synthesis of nanocomposites.

In the present melt mixing technique 10 gm of PP was heated at 200°C for 15 minutes and BaCO_3 nano powder with various concentrations of 1%, 3%, 5% and 10% weight of PP were mixed. The obtained mixtures were stirred for 15

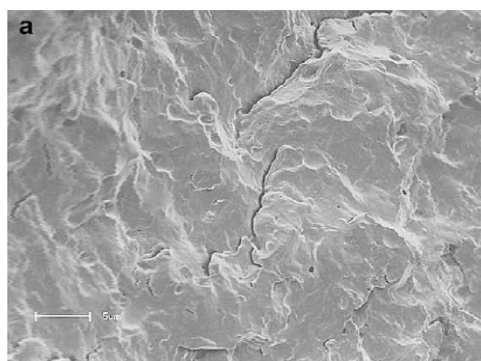
minutes, later on cooled for solidification. The solidified products were characterized by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) for structural conformation.

Thermal and crystallization behavior of the nanocomposites were studied using Differential Scanning Calorimeter (DSC Q20 V24.10 Build 122) and Thermo gravimetric Analysis instrument (TGA Q 50 V20.13 Build 39). For DSC studies about 3.5 mg. of the sample is heated from 40 to 600°C at a heating rate of 10°C per minute in air. For TGA studies about 10mg. of sample is heated from 30 to 800°C at a heating rate of 10°C per minute in air.

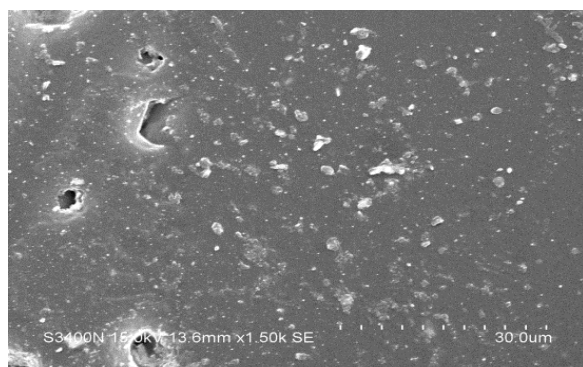
RESULTS AND DISCUSSIONS

Surface Morphology

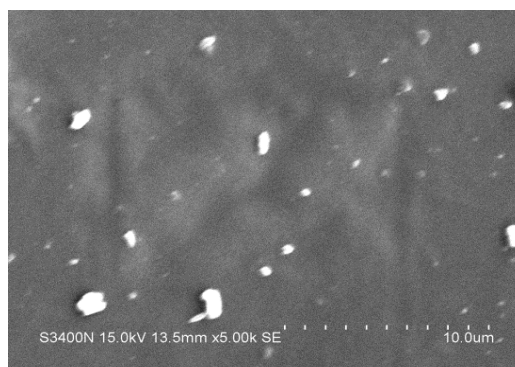
Scanning electron microscopy (SEM) is employed to study the morphology to investigate the impact fracture surfaces of the nanocomposites by Hitachi Model S4700. Well dispersed nano particles can have a significant effect on the mechanical properties of the nanocomposites [28, 29]. Morphology of nano composites has been evaluated by scanning electron microscopy (SEM) to observe the dispersion of nanoparticles within the polymer. SEM images of 1%, 3%, 5% & 10% weight of PP are presented in figures from 1(a) to 1(e), which depict the micro graphs of a fractured surface of the nanocomposites for the filler contents. The fractured surface of pure PP is found to be smooth and featureless[26], but fairly good nano particle dispersion is seen in the micro graphs of PP with filler loadings of 1%, 3%, 5% & 10% weight of PP.



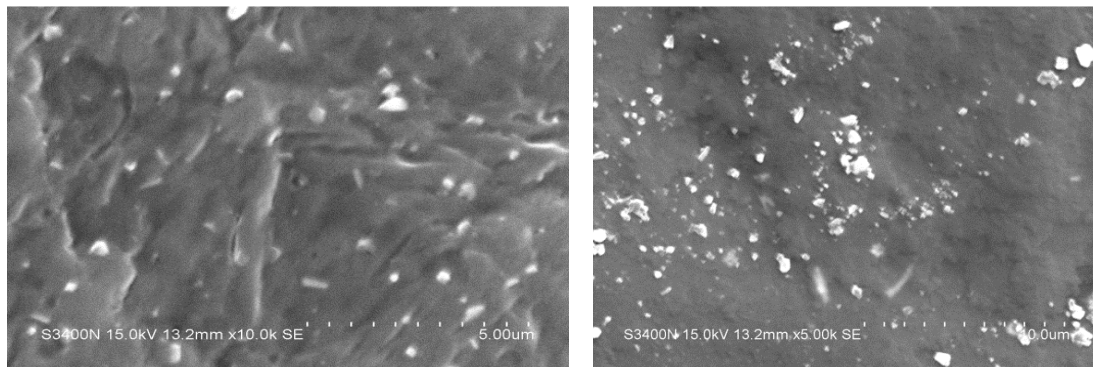
1(a) SEM Image of Pure PP



1(b) SEM Image of PP+1% BaCO₃ (NPBC)



1(c) SEM Image of PP+3% BaCO₃ (NPBC)



1(d) SEM Image of PP+5% BaCO₃ (NPBC) 1 (e) SEM Image of PP+10% BaCO₃ (NPBC)

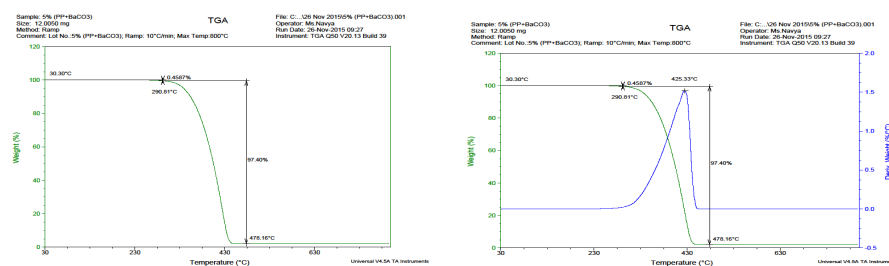
Figure 1

A good dispersion of nanoparticles is found for the nanocomposites containing 5% w/w BaCO₃ nano particles when compared to other filler loadings of PP. With filler content of 10% w/w, aggregates of nano particles are found. The SEM images were analyzed and it has been confirmed that the filler particle sizes are in nano metric scale [30].

THERMAL AND CRYSTALLIZATION STUDIES

Thermo gravimetric Analysis (TGA)

Thermal stability of thermo plastic-based polypropylene polymer nanocomposites has been investigated using thermo gravimetric analysis (TGA) with an atmosphere of air with linear temperature ramp of 10⁰c/min. Typical TGA thermo grams and corresponding derivatives of the nanocomposites with filler loadings of 1%, 3%, 5% & 10% wt. of PP are shown in figures 2(a) to 2(d). It is observed that initial degradation temperature (T_i) is not effected with the incorporation of nanoparticles in the polymer matrix. A single phase degradation smooth curves are found, they are representing the homogeneity of nanocomposites. In fact there are two ways to describe the oxidation temperature, the weight loss onset temperature (T_{onset}) and the temperature of the maximum in the weight loss rate (dm/dT_{max}). As T_{onset} is ambiguous and determining dm/dT_{max} is relatively straight forward, in the present study the oxidation temperature $T_o = dm/dT_{max}$ has been considered for the determination of thermal stability of the polymer nanocomposites. The oxidation values obtained from the derivative graphs for filler loadings NPBC 1%, 3%, 5% & 10% wt. of PP are 433.65⁰c, 435.16⁰c, 425.33⁰c & 434.41⁰c respectively. A considerable reduction in the oxidation value i.e.; 425.33⁰c for PP+5%NPBC has been noted, when compared to other composites. Oxidation temperature T_o , is basically a measure of the thermal stability of nanocomposites in air. Higher oxidation temperature is always associated with purer, the lower values of T_o for PP+5%NPBC has emphasized the well dispersion of nanoparticles and de-bonding of the polymer matrix.



2(a)

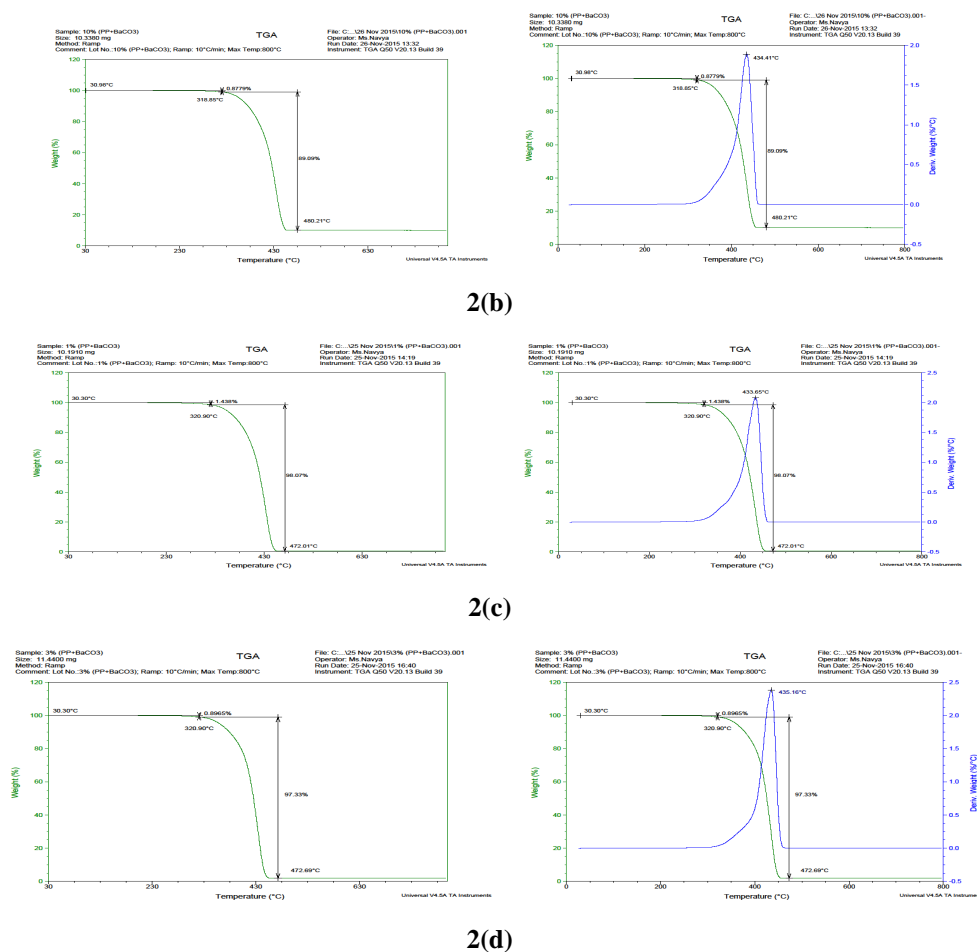


Figure 2: TGA Thermograms & their First Derivatives of (a) PP+1% BaCO₃ (b) PP+3% BaCO₃ (c) PP+5% BaCO₃ & (d) PP+10% BaCO₃

Differential Scanning Calorimetry (DSC)

It is a well known fact that the crystalline morphology and structure obtained during thermoplastic processing plays an important role on the physico-mechanical behavior of the resulting polymeric material, conditioning its potential uses. In this way, the control of the crystallization process can be seen as a successful approach for improving physico-mechanical properties of polymers. Therefore it is of great interest to investigate the nucleation, crystallization and structural development of the matrix in nanoparticle metallic carbonates reinforced polymer nanocomposites [31]. This would help to optimize the manufacturing conditions in order to fully exploit their potential in practical applications. PP is a type of typical semi crystalline polymer and the crystallization behavior of PP significantly influences its mechanical characteristics. Hence investigation of the thermal properties is significant both from theoretical as well as practical points of view. The data related to thermal properties of PP+BaCO₃ nano composites include crystallization temperature (T_c), melting temperature (T_m), degree of crystallinity (χ_c). Typical DSC thermograms for neat iPP and composites reinforced with 1%, 3%, 5% & 10% wt. of PP are shown in figures 3(a) to 3(d).

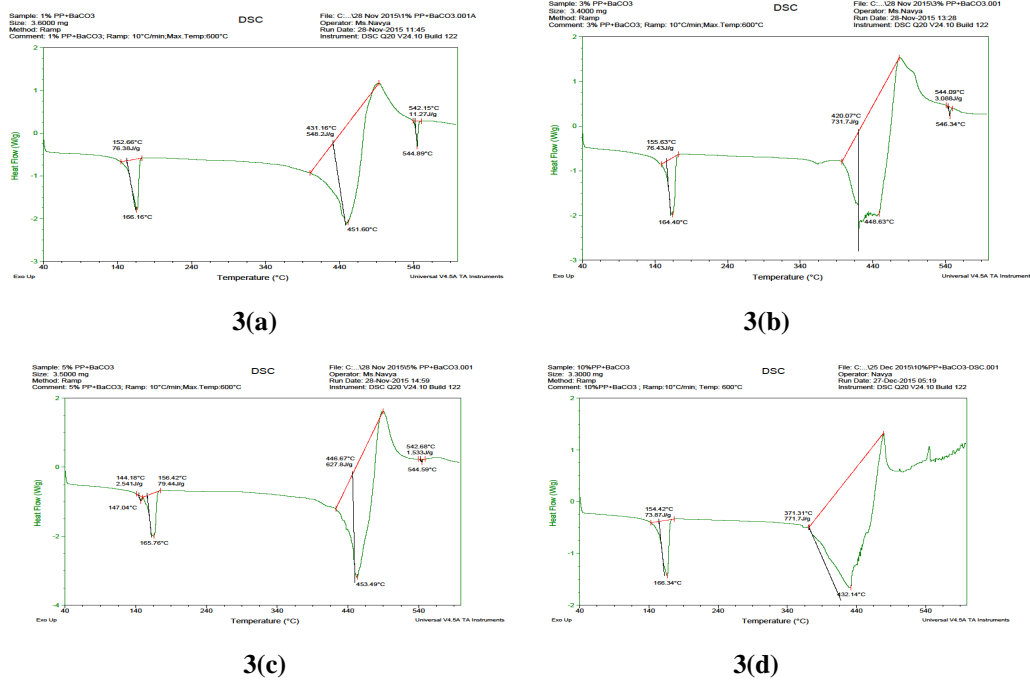


Figure 3: DSC Thermograms of (a) PP+1% BaCO₃ (b) PP+3% BaCO₃ (c) PP+5% BaCO₃ & (d) PP+10% BaCO₃

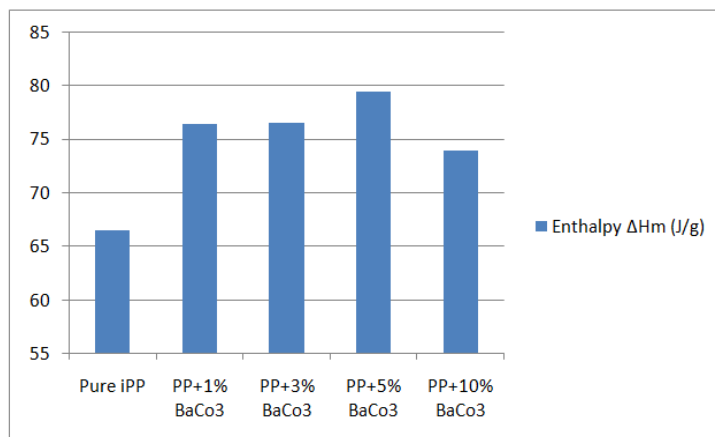
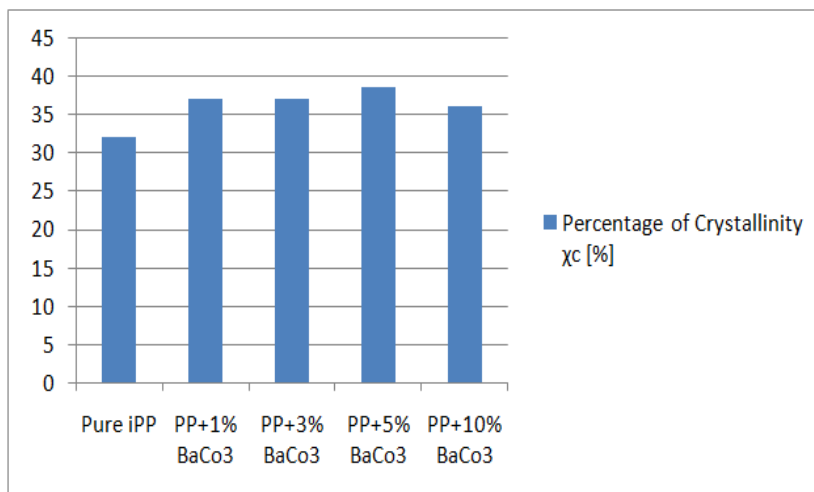
Differential Scanning Calorimetry (DSC) analysis has been carried out to the pure form of isotactic polypropylene (iPP) and the composites of iPP filled with nano particle barium carbonate (NPBC). The peak temperatures of the thermograms considered as the melting temperatures of the polymer PP. The peak area was taken into consideration for determining the melting enthalpy. The studies of A. Buasri et al; revealed that T_m of pure PP is about 164.75°C [32]. It should be noted that melting enthalpy (ΔH) values shown have been corrected for filler content, thus expressed in J/g for polymer PP. The percentage of crystallinity of nano samples were then calculated using ΔH values, taken 207.1 J/g as the theoretical enthalpy value for a 100% crystalline PP [33]. The degree of crystallinity (χ_c) is a key parameter in thermoplastic polymers as it has strong influence on both chemical and mechanical characteristics. The crystalline phase can improve the stiffness and tensile strength while the amorphous phase is significant in absorbing the impact energy. The research studies by A. Akinici [33] revealed that the T_m of PP is 163.73°C, ΔH_m 66.43 J/g and χ_c, 32% are presented in table-1. While the studies of M. Y. A. Faud et al; [27] revealed that the T_m of PP is 163°C, ΔH_m 78 J/g and χ_c 37%. The parametric values of the composites of PP with 1%, 3%, 5% and 10% BaCO₃ (NPBC) viz; melting temperature (T_m); enthalpy (ΔH_m) and percentage of crystallinity (χ_c%) of polypropylene and BaCO₃ are presented in table-1. The crystallization of iPP and nucleation activity of the filler were calculated by using the relationship

$$\chi_c = \frac{\Delta H_m(\frac{m_c}{m_p})}{\Delta H_0} \times 100$$

- **Where ΔH_m:** Melting enthalpy measured in heating experiments ;
- **ΔH₀:** Theoretical value of enthalpy of 100% crystalline PP (standard value of ΔH₀ = 207.1 J/g),
- **m_c:** Mass of the sample and
- **m_p:** Mass of iPP in the sample.

Table 1: Details of DSC Thermal Characteristics of Polypropylene and BaCO₃

Composite (Sample)	Polypropylene (PP)			BaCO ₃	
	Melting Temperature T_m [$^{\circ}$ C]	Enthalpy ΔH_m [J/g]	Percentage of Crystallinity X_c [%]	Melting Temperature T_m [$^{\circ}$ C]	Enthalpy ΔH_m [J/g]
Pure iPP	163.73	66.43	32	---	---
PP+1% BaCO ₃	166.16	76.38	36.91	544.89	11.27
PP+3% BaCO ₃	164.40	76.43	37.01	546.34	3.088
PP+5% BaCO ₃	165.76	79.44	38.55	544.59	1.533
PP+10% BaCO ₃	166.34	73.87	36.03	---	---

Figure 4: Enthalpy ΔH_m (J/g)Figure 5: Percentage of Crystallinity X_c [%]

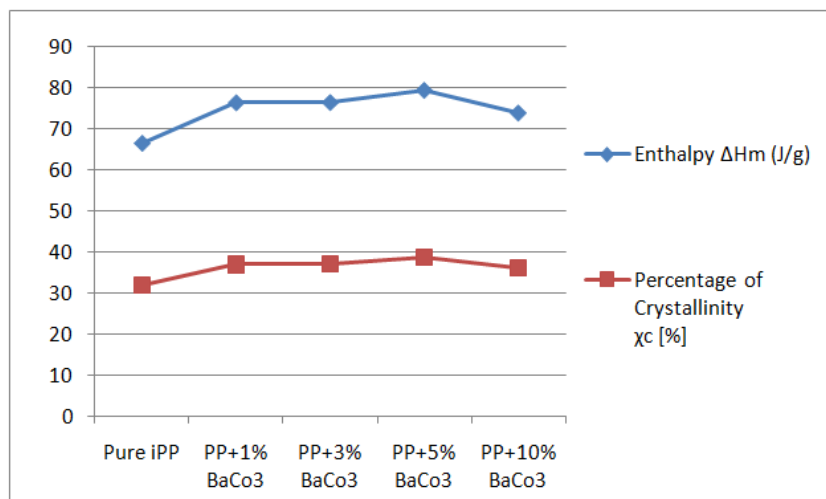


Figure 6

CONCLUSIONS

In summary, thermal studies are carried out successfully for PP/BaCO₃ nanocomposites. The TGA curves have emphasized the homogeneity of nanocomposites. The results of DSC tests showed that melting temperature of host polymer matrix is not affected by the filler loadings of nanoparticles, where as a significant change in enthalpy (ΔH_m) and percentage of crystallinity have been observed. It has been noted that enthalpy polymer composite increased up to 5% weight of NPBC in polymer, latter it is declined. A similar change is also found in the percentage of crystallinity. During melting process polymer chains fall out of their crystal structure and become disordered liquid. For the nanocomposite PP+5%NPBC high melting enthalpy, 79.44J/g has been noted, compared to other composites. So during the first order transition the composite has absorbed high thermal energy. It suggests the good adhesion/ inter-molecular bonding between the nanoparticles and the polymer matrix. It is a good sign of stability and crystallinity. It has also been found the crystallinity of 38.55% for the nanocomposite of the polymer at the filler loading of 5% weight of PP, the maximum of the tabulated values. A good dispersion of nanoparticles was also found at the filler loading of 5% wt. of NPBC in the polymer matrix which was depicted in Figure 1 (d). The well dispersed nanoparticles act as stress concentrators and load bearing centers' which supports the present obtained results. Hence it can be concluded that polypropylene incorporated with Barium carbonate nanoparticles with 5% weight of the polymer can be a good thermoplastic nanocomposite can exhibit good tensile strength, rigidity modulus etc; mechanical properties. Much work remains to be done, in order to examine the mechanical properties of PP/BaCO₃ nanocomposites.

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